

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Appl. No. : 10/719,381
Applicant (s) : Cady et al.
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TC/A.U. : 1713
Examiner : R.D. Harlan
Title : SHEAR THINNING ETHYLENE/ α -OLEFIN INTERPOLYMERS
AND THEIR PREPARATION
Docket No. : DW0029USCNT
Customer No. : 00109

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R § 1.132

I, ROBERT J. JORGENSEN, declare and state the following:

- (1) I am a Research Leader in Gas Phase PE Research at the Union Carbide Corporation ("UCC"), a wholly owned subsidiary of The Dow Chemical Company, 3200/3300 Kanawha Turnpike, South Charleston, West Virginia. I have been continuously employed by the Union Carbide Corporation, now a wholly owned subsidiary of The Dow Chemical Company ("DOW"), in process and catalyst research in gas phase polymerization for 30 years.
- (2) I received a Ph.D. degree in Chemical Engineering from the University of Massachusetts, Amherst, in 1978.
- (3) UCC became a subsidiary of DOW in February 2001.
- (4) I am currently responsible for Gas Phase Polymerization Process Research, including catalyst development, primarily in the area of polyethylene. I am the inventor/co-inventor on about 30 U.S. patents. Most of my patents and publications are directed to improvements in gas phase polymerization processes and catalysts used in these processes.

- (5) I have worked in the area of organometallic catalysts for more than 30 years. I am familiar with the structures and catalytic mechanisms of Ziegler-Natta catalysts systems, metallocene catalyst systems and constrained geometry catalyst systems.
- (6) I have examined U.S. Patent 4,343,755 to Miller et al. (hereinafter the '755 patent). I assisted in the coordination of pilot plant polymerizations of two ethylene/butene copolymers, using parameters described for Example 3 (see Tables A and B) of the '755 patent, as discussed below.
- (7) Each copolymer was polymerized using a catalyst, second generation to that of the catalyst described in the '755 patent (see column 20, line 54 to column 24, line 9). Both the catalyst described in the '755 patent, and the second generation catalyst of the '755 catalyst, are Ziegler-Natta type catalysts that produce linear ethylene/ α -olefin copolymers that do not have measurable amounts of long chain branching. In addition, the catalysts disclosed in the '755 patent (for example, see column 8, line 21 to column 13, line 18; and column 20, line 54 to column 24, line 9) produce linear ethylene/ α -olefin copolymers that do not have measurable amounts of long chain branching.
- (8) The second generation catalyst differs from the catalyst described in the '755 patent in the following respects.
- (i) The titanium compound utilized in the formation of the catalyst precursor was $\text{TiCl}_3(1/3 \text{ AlCl}_3)$ instead of TiCl_4 . It was found that, in the subsequent preactivation of the catalyst with aluminum alkyl, as described in the example in the '755 patent (see columns 20 and 21 (I. Preparation of Impregnated Precursor)), a substantial improvement in catalyst productivity could be achieved, although the basic polymer structure does not change. The catalyst preparation procedure used (excluding specific amounts of activating agents added), is similar to that described in U.S. Patent 4,710,538, Example 1, attached herewith.

(ii) Additionally, this change in catalyst precursor resulted in better polymer particle shape, a desirable feature in gas phase fluidized bed polymerizations, again, without changing the polymer structure.

However, as discussed above, both catalysts produce copolymer with similar branching distribution, that is, linear ethylene/ α -olefin copolymers that do not have measurable amounts of long chain branching. The second generation catalyst also has a better response to hydrogen as chain transfer agent, as indicated by the lower viscosity of the copolymer prepared in Run 1, as discussed below. This effect (better hydrogen chain transfer response with higher activity catalysts) is generally known in the art.

- (9) Two pilot plant polymerizations (Run 1 and Run 2) were run to provide two ethylene/butene-1 copolymers, representative of the branching distribution of the Example 3 (or Run No. 3) copolymer disclosed in the '755 patent (see Tables A and B). As discussed above, the difference in the polymerization rates, and termination rates between the second generation catalyst and the catalyst disclosed in the '755 patent, will account for differences in the molecular weight of the final copolymer product.
- (10) The first copolymerization (Run 1) resulted in Copolymer 1, and was run using essentially the same gas ratios, as shown for Example 3 in Table A of the '755 patent. These ratios included the following: H_2/C_2 mole ratio of 0.145 to 0.155 and C_4/C_2 mole ratio of approximately 0.44. In addition, ethylene, C_2 , was present at approximately 180 psi partial pressure, and the reaction temperature was 85°C. Total reactor pressure was approximately 350 psig, the remainder being inerts such as nitrogen. Triethylaluminum was used as the final activation agent for the catalyst in the fluidized bed reactor. An added Al/Ti mole ratio of approximately 100 was used.
- (11) The second generation catalyst used, available from Univation Technologies, was a UCAT® Catalyst A4520. This is a silica supported catalyst comprising

a 3/1 mole ratio of MgCl_2 to TiCl_3 (1/3 AlCl_3) with Tetrahydrofuran (THF) present as an electron donor. This catalyst is made in a similar multi-step process as described in the '755 patent. The partial activation procedure is performed in the same manner, however the partial activation of the second generation catalyst uses sequential addition of Diethylaluminum Chloride (added at a 0.45/1 molar ratio to the THF present in the "precursor" composition) followed by addition of Tri-n-hexylaluminum (at a 0.2/1 molar ratio to the THF). The final catalyst contains ~ 12 wt% THF, 1.1 wt% Ti and has a total added Al/Ti mole ratio of ~5.2 to 5.5.

- (12) Actual average reaction conditions and product properties for both Run 1 and Run 2 (discussed below) are shown in the Table 1 below.

Table 1

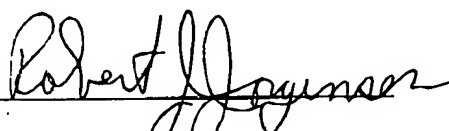
		Run 1 (Copolymer 1)	Run 2 (Copolymer 2)
Reaction Conditions			
Bed Temp	C	85	85
C2 PP	psi	180	180
H2/C2	mol/mol	0.15	0.11
C4/C2	mol/mol	0.439	0.265
Cocatalyst		TEAL	TEAL
Resin Properties			
Melt Index (I2)	dg/10 min	1.55	0.59
Density	g/cc	0.918	0.925
MFR	I21/I2	26.5	25.4
Ti	ppm	1.29	1
Al	ppm	75	50
Al/Ti	mol/mol	103	91
APS	inch	0.0464	0.0497

- (13) The copolymer produced in Run 1 had a Melt Index of 1.55. This is indicative of a lower molecular weight copolymer, and this, in turn, indicates that the second generation catalyst reacts with hydrogen at a faster rate to terminate growing polymer chains. Melt index and Density were measured using standard ASTM methods as in the (density measured according to ASTM-D-792 and melt index (I2) according to ASTM D-1238-Condition E).

- (14) The second copolymerization (Run 2) resulted in Copolymer 2, and was run using adjusted gas ratios to produce a copolymer with a density and melt index, similar to those listed for Example 3, in Table B of the '755 patent. The copolymer had a density of 0.925 g/cc, and a melt index, I2, of 0.59 g/10 min (see Table 1 above).

The undersigned declares further that all statements made herein of his own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements, and the like, so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date 8-15-06


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